Pestic. Sci. 1996, **48**, 189–196

The Synthesis and Insecticidal Activity of a Series of 2-Aryl-1,2,3-triazoles

Ian K. Boddy, Geoff G. Briggs, Richard P. Harrison, Tim H. Jones, Mary J. O'Mahony,* Ian D. Marlow, Brian G. Roberts, R. John Willis, Richard Bardsley & Jim Reid

AgrEvo UK Limited, Chesterford Park, Saffron Walden, Essex, CB10 1XL, UK

(Received 11 July 1995; revised version received 22 January 1996; accepted 12 June 1996)

Abstract: Two synthetic routes to 2-aryl-1,2,3-triazoles are outlined. These have been used to synthesise a wide range of compounds of this structural type. Their insecticidal activities were evaluated against a number of veterinary and public health pests. The activity of these compounds is especially good against the housefly (*Musca domestica*). Structure–activity relationships are discussed particularly in relation to the physical properties of the compounds.

Key words: insecticide, 2-aryl-1,2,3-triazoles, synthesis, structure–activity relationship, physical properties

1 INTRODUCTION

Recent publications on 1-arylpyrazoles and 1-arylpyrimidinones indicate their potential for high insecticidal activity.[1–3] We wish to report our work on 2-aryl-1,2,3-triazoles in which a range of compounds was synthesised to optimise activity against veterinary and public health insects represented by sheep blowfly (*Lucilia sericata* Meig), housefly (*Musca domestica* L.), ticks (*Boophilus microplus* Can.) and cockroaches (*Blattella germanica* L.).[4]

2 EXPERIMENTAL

2.1 Synthesis

Representative syntheses are described below. Where possible starting materials were obtained from commercial suppliers. Melting points were measured on a hot plate apparatus and are uncorrected. All compounds described gave [^{1}H]NMR, MS, infra-red and micro-analytical data consistent with the proposed structures.

The two synthesis routes employed are outlined in Figs 1 and 2, and a selection of the compounds prepared by these methods is shown with melting points in Tables 1 and 2.

Reaction of an arylhydrazine with the keto-oxime **1** yields the oximinohydrazono compound **2** which cyclises readily under copper catalysis to give the triazole *N*-oxide **3**. Methylation of the *N*-oxide and reaction with a suitable nucleophile gives the desired product, **4**. (Route A; Fig. 1). This route is based on chemistry developed by Begtrup.[5–7]

The second route is illustrated in Fig. 2 and involves reaction of the appropriate arylhydrazine with the bis-oxime **5** to give the hydrazone **6**. Mono acetylation and cyclisation with either potassium carbonate or caesium carbonate gives the triazole-4-carbaldoxime **7**.[8] Subsequent hydrolysis to the triazole-4-carbaldehyde, **8**, followed by sodium borohydride reduction yields the hydroxymethyl compound **9** which may be further functionalised *via* methanesulfonate formation and displacement with suitable nucleophiles.

Compounds **22–24** were prepared using a variation of the latter route. The oxime functionality was introduced into acetoacetanilide *via* nitrosation. Hydrazone formation, acetylation of the oxime and cyclisation with caesium carbonate yielded 2-(2,6-dichloro-4-trifluoromethylphenyl)-5-methyl-*N*-phenyl-2*H*-1,2,3-triazole-4-carboxamide. Hydrolysis of the amide gave the corresponding carboxylic acid, and standard functional group interconversions gave the required compounds.

* To whom correspondence should be addressed.

Pestic. Sci. 0031-613X/96/$09.00

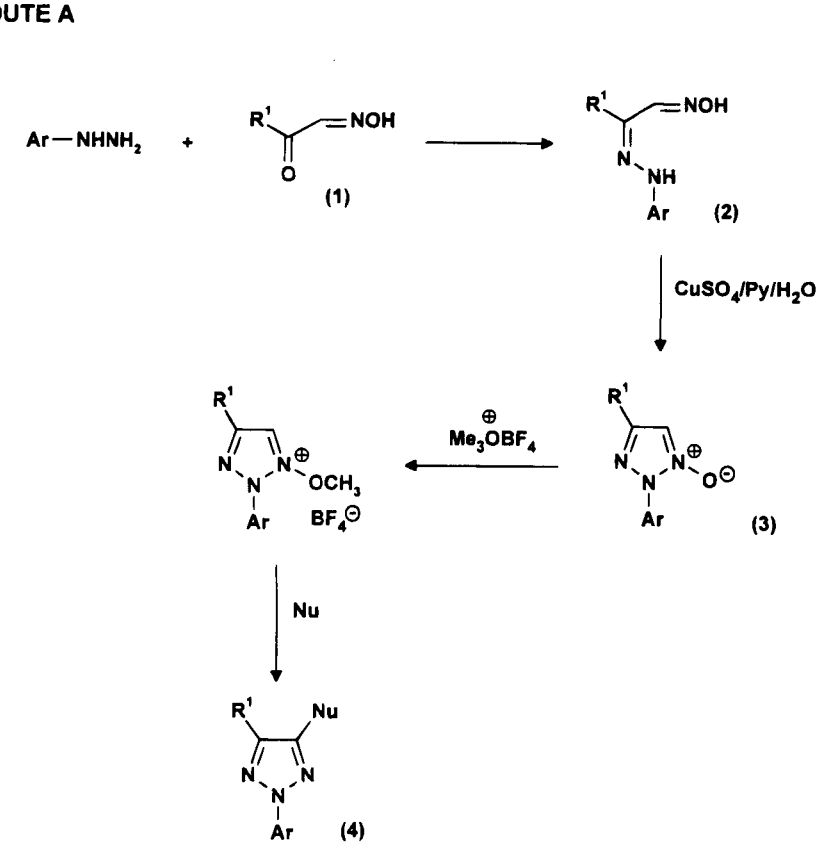


Fig. 1. Route A to substituted 2-aryl-1,2,3-triazoles.

Compounds containing alkylthio groups were further modified by oxidation (i.e. compounds **13**, **14**, **23**, **35** and **36**).

Haloalkylthio substituted compounds were formed *via* alkylation of the free thiol compound formed by hydrolysis of the corresponding thioacetate compound (e.g. compounds **16**, **17** and **32**).

The triazole carbaldehyde **8** shown in Fig. 2 was further elaborated to the difluoromethyl compound **30** and the nitrile **29**.

2.1.1 Route A (Fig. 1)

A solution of 2,6-dichloro-4-trifluoromethylphenylhydrazine (20 g, 0·081 mol) in diethyl ether (75 ml) was added with cooling to a solution of 2-oxopropanal 1-oxime (7·1 g, 0·082 mol) in ether (75 ml) at 0°C. The mixture was stirred at room temperature overnight and magnesium sulfate and charcoal added. The mixture was filtered and the solvent evaporated under reduced pressure. The residue was purified by column chromatography using ether + light petroleum distillate (1 + 5 by volume) to give 2-(2,6-dichloro-4-trifluoromethylphenylhydrazono)propanal 1-oxime, (26·6 g, 100%) as a colourless solid, m.p. 138–139°C. ν_{max} (potassium bromide disc) cm^{-1} 1520, 1575, 1605. δ_H (300 MHz; deuterochloroform) 2·1 (3H, s, CH_3), 7·55 (2H, brs, exch in D_2O, NH and OH), 7·85 (1H, s, C*H*NOH); *m/z* (%) 313/5 (M^+, 5), 296/8 (5), 229 (40), 59 (100).

Copper sulfate (15 g, 0·03 mol) in water (60 ml) was added dropwise to a solution of this product (9·4 g, 0·06 mol) in pyridine (120 ml) and the mixture stirred at room temperature overnight. The reaction was cooled, acidified with concentrated hydrochloric acid (135 ml) and extracted with diethyl ether. The ether extract was dried and evaporated under reduced pressure and the product purified by column chromatography using ether + light petroleum distillate (4 + 1 by volume) to give 2-(2,6-dichloro-4-trifluoromethylphenyl)-4-methyl-2*H*-1,2,3-triazole 1-oxide, (8·4 g, 90%) as a colourless solid, m.p. 134–136°C. ν_{max} (potassium bromide disc) cm^{-1} 1530, 3110. δ_H (300 MHz; deuterochloroform) 2·35 (3H, s, CH_3), 7·3 (1H, s, H_5), 7·25 (2H, s, arH); *m/z* (%) 311/3 (M^+, 10) 276 (15), 246 (25), 227 (40), 213 (60).

A solution of this compound (8·4 g, 0·027 mol) and trimethyloxonium tetrafluoroborate (6·0 g, 0·04 mol) in dichloromethane (85 ml) was stirred at room temperature for three days. Dry diethyl ether (50 ml) was added and the precipitated methoxytriazolium salt collected by filtration under nitrogen. This salt (2·15 g, 0·005 mol) was added in portions to a solution of sodium methanethiolate (0·42 g, 0·006 mol) in methanol (15 ml), keeping the temperature at 15–20°C. After stir-

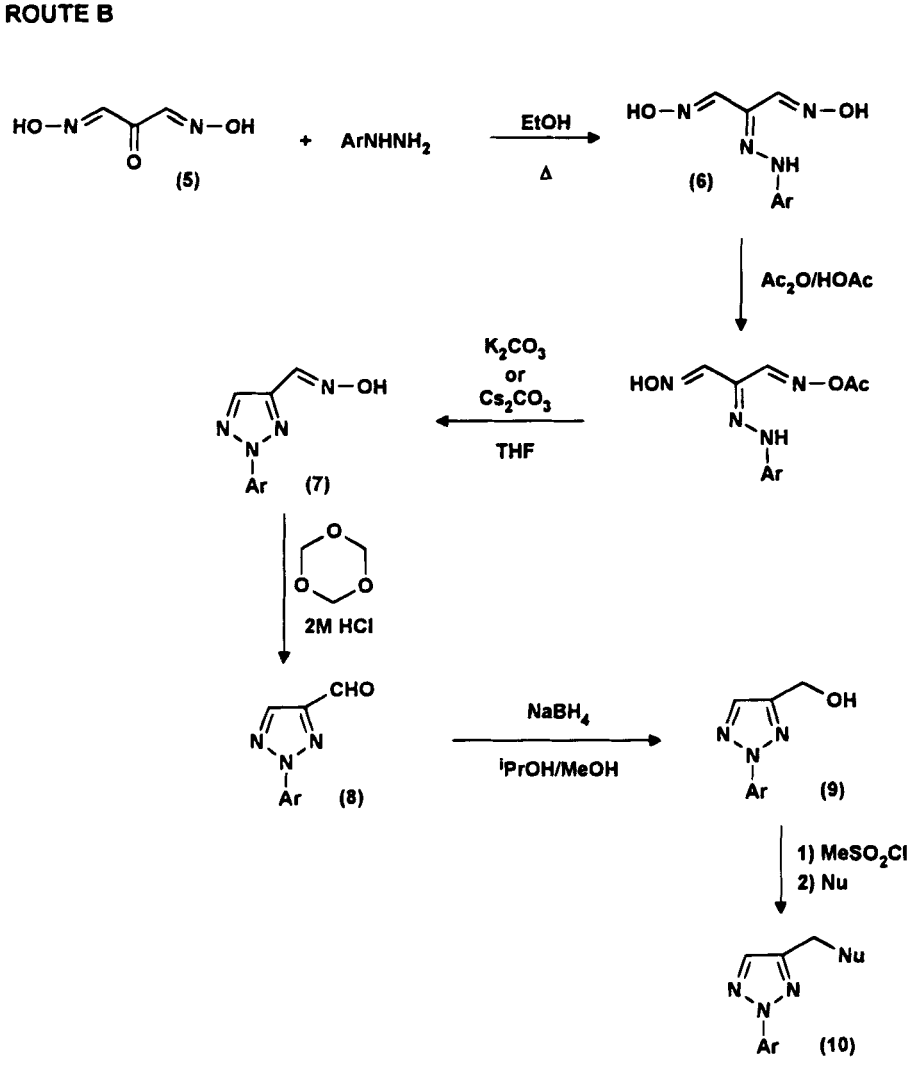


Fig. 2. Route B to substituted 2-aryl-1,2,3-triazoles.

ring for 30 min at room temperature, the solvent was evaporated under reduced pressure and the residue extracted with ether. The extract was evaporated and the residue purified by column chromatography using ether + light petroleum distillate (3 + 97 by volume) to give 2-(2,6-dichloro-4-trifluoromethylphenyl)-4-methyl-5-methylthio-2*H*-1,2,3-triazole, compound **12**, (1·2 g, 70%) as a colourless oil which crystallised on standing, m.p. 38–40°C. δ_H (300 MHz; deuterochloroform) 2·25 (3H, s, CH_3) 2·5 (3H, s, SCH_3), 7·6 (2H, s, arH); *m/z* (%) 341/3 (M^+, 65), 308 (60), 227 (100).

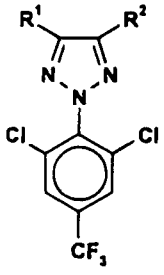
2.1.2 Route B (Fig. 2)

A mixture of 2,6-dichloro-4-trifluoromethylphenylhydrazine (34 g, 0·139 mol), 2-oxopropanedial 1,3-dioxime (17 g, 0·146 mol) and ethanol (300 ml) was heated under reflux for 2 h. The solvent was evaporated under reduced pressure and the residue triturated with light petroleum distillate (b.p. 40–60°) and filtered to give 2-oxopropanedial 2-(2,6-dichloro-4-trifluoromethylphenylhydrazone) 1,3-dioxime (36 g, 76%) as a colourless solid, m.p. 177–179°C. δ_H (300 MHz, hexadeuteroacetone) 7·75 (2H, s, arH), 7·8 (1H, s, C*H* = NOH), 8·4 (1H, s, C*H*NOH), 10·6 (1H, brs), 11·5 (1H, brs), 12·3 (1H, brs), 2 × OH + 1 × NH.

This product (36 g, 0·106 mol) was stirred in acetic anhydride (350 ml) and acetic acid (220 ml) at room temperature for 45 min. This mixture was poured into water and the precipitated solid collected and dried at 40° to give 2-oxopropanedial 1-(*o*-acetyloxime) 2-(2,6-dichloro-4-trifluoromethylphenylhydrazone) 3-oxime (38·5 g, 95%) as a solid, m.p. 180–182°C. δ_H (300 MHz, hexadeuterodimethylsulfoxide) 1·95 (3H, s, CH_3), 8·3 (2H, s, arH), 8·35 (1H, s, C*H*NOH), 8·5 (1H, s, C*H*NOAc), 11·85 and 11·9 (2H, 2brs, NH + OH).

A mixture of this product (38·5 g, 0·1 mol) and caesium carbonate (32·6 g, 0·1 mol) in tetrahydrofuran (1000 ml) was stirred at room temperature for 1 h. The

TABLE 1
Physical Properties of 2-(2,6-Dichloro-4-trifluoromethylphenyl)-1,2,3-triazoles



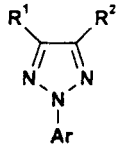
Compound number	R^1	R^2	*m.p.* (°C)	*Synthetic route*
11	CH_3	CN	52	A
12	CH_3	SCH_3	38–40	A
13	CH_3	SO_2CH_3	87–89	A
14	CH_3	$SOCH_3$	Oil	A
15	CH_3	SCH_2F	Oil	A
16	CH_3	$SCHF_2$	33–35	A
17	CH_3	$SCBrF_2$	46–48	A
18	CH_3	SCH_2CH_3	Oil	A
19	CH_3	$SCH(CH_3)_2$	Oil	A
20	CH_3	$SC(CH_3)_3$	79–81	A
21	CH_3	SC_6H_5	78	A
22	CH_3	CH_2SCH_3	65–67	B
23	CH_3	$CH_2SO_2CH_3$	67–68.5	B
24	CH_3	CH_2CN	103–104	B
25	CH_3	OCH_3	64–66	A
26	CH_3	$N(CH_3)_2$	68–69	A
27	CH_3	$SO_2N(CH_3)_2$	89–91	A
28	H	SCH_3	100–101	A
29	H	CN	51–53	B
30	H	CHF_2	36–37	B
31	H	CH_2SCH_3	65–67	B
32	H	CH_2SCHF_2	32–33	B
33	H	$CH_2SCH_2CH_3$	53–54	B
34	H	$CH_2SCH_2C_6H_5$	67–68	B
35	H	CH_2SOCH_3	140–142	B
36	H	$CH_2SO_2CH_3$	165–168	B
37	C_2H_5	SCH_3	51–52	A
38	$CH(CH_3)_2$	SCH_3	Oil	A
39	$C(CH_3)_3$	SCH_3	Oil	A
40	H	$C(CH_3)_3$	60	B
41	H	NO_2	105	B

solvent was evaporated under reduced pressure and the residue taken up in diethyl ether. The extract was washed with water, dried and evaporated. The residue was triturated with light petroleum distillate (b.p. 40–60°C) and filtered to give 2-(2,6-dichloro-4-trifluoromethylphenyl)-2*H*-1,2,3-triazole-4-carbaldehyde oxime (26·7 g, 82%) as a solid (mixture of two isomers), m.p. 105–107°C. δ_H (300 MHz; deuterochloroform) 7·75 (2H, 2s, arH), 7·8, 8·2, 8·35, 8·65 (2H, 4s, C*H*NOH + H_5) 9·20 (1H, brs, OH).

This oxime (26·3 g, 0·088 mol) and 1,3,5-trioxane (80 g, 0·89 mol) in hydrochloric acid (2M; 1000 ml) were heated to reflux for 6 h. The mixture was cooled and extracted with diethyl ether. The organic extract was washed with water, dried and evaporated to give 2-(2,6-dichloro-4-trifluoromethylphenyl)-2*H*-1,2,3-triazole-4-carbaldehyde (21·5 g, 86%) as a pale yellow solid, m.p. 94–95°C. δ_H (300 MHz, deuterochloroform) 7·80 (2H, s, arH), 8·4 (1H, s, H_5), 10·25 (1H, s, CHO).

Sodium borohydride (0·67 g, 0·0177 mol) was added in portions to a solution of the triazole carbaldehyde (5 g, 0·016 mol) in isopropanol (50 ml) and methanol (20 ml). The reaction mixture was stirred at room temperature overnight. Water (15 ml) was added, and the

TABLE 2
Physical Properties of 2-Aryl-1,2,3-triazoles



Compound number	R^1	R^2	*Ar*	*m.p. (°C)*	*Synthetic route*
42	CH_3	SCH_3	2,4,6-Cl_3	87·5–90	A
43	CH_3	SCH_3	2,6-Br_2, 4-CF_3	56–58	A
44	CH_3	SCH_3	2,3,4,5,6-F_5	Oil	A
45	CH_3	SCH_3	2,3,5,6-F_4, 4-CF_3	Oil	A
46	CH_3	SCH_3	2,6-Cl_2, 4-SCF_3	58–60	A
47	H	CH_2SCH_3	2,6-Cl_2, 4-OCF_3	67·5–70	B
48	H	CH_2SCH_3	2,4,6-Cl_3	38–40	B

mixture acidified with concentrated hydrochloric acid. The solution was poured into water (250 ml) and extracted with diethyl ether. The extract was washed with brine, dried and evaporated under reduced pressure to give [2-(2,6-dichloro-4-trifluoromethylphenyl)-2*H*-1,2,3-triazol-4-yl]methanol (4·6 g, 92%) as a white solid, m.p. 87–88°C). δ_H (300 MHz, deuterochloroform) 4·55 (1H, t, OH), 4·80 (2H, d, CH_2), 8·05 (1H, s, H_5), 8·10 (2H, s, arH).

Methanesulfonyl chloride (0·54 g, 0·005 mol) was added dropwise to a solution of the triazole alcohol (1·5 g, 0·0005 mol) and triethylamine (0·66 ml) in tetrahydrofuran (30 ml). After stirring for 40 min at room temperature, the mixture was poured into water and extracted with diethyl ether. The extract was dried and evaporated and the residue triturated with light petroleum distillate (b.p. 40–60°C) to give [2-(2,6-dichloro-4-trifluoromethylphenyl)-2*H*-1,2,3-triazole-4-yl]methyl methanesulfonate (1·5 g, 80%) as a white solid, m.p. 96–97°C.

Sodium methanethiolate (0·34 g, 0·005 mol) was added to a solution of the triazole mesylate (1·83 g, 0·005 mol) in acetonitrile (20 ml). The mixture was stirred at room temperature for three days, then poured into water and extracted with diethyl ether. The ether extract was dried and evaporated and the residue purified by column chromatography using ether + hexane (1 + 9 by volume) to give 2-(2,6-dichloro-4-trifluoromethylphenyl) - 4 - (methylthiomethyl) - 2*H* - 1,2,3 - triazole(0·9 g, 56%) as a white solid, m.p. 65–67°C). δ_H (300 MHz, deuterochloroform) 2·10 (3H, s, SCH_3), 3·85 (2H, s, CH_2S), 7·75 (2H, s, arH), 7·95 (1H, s, H_5). *m/z* (%) 341/3 (M^+, 10), 295/7 (100).

2.2 Biological evaluation

Each of the compounds synthesised was tested for biological activity against ticks (*B. microplus*) in both a larval contact test and a gravid female injection test assessing reproductive viability. Insecticidal activity was assessed against sheep blowfly (*L. sericata*) as a larval test using first-instar larvae and housefly (*M. domestica*) using adult flies. When good activity was noted for those species, cockroaches (*B. germanica*) were assayed as a contact test using first-instar nymphs.

Representative tests are outlined below for each of these insect and acarine species. In all cases, control experiments led to less than 5% mortality/reduction in reproductive capacity.

2.2.1 *Tick* (Boophilus microplus)

Larval test. Filter papers (9 cm diameter) were impregnated with 1-ml aliquots of acetone solutions or suspensions of test compound at various concentrations (300, 100, 30, 10, 3 mg $litre^{-1}$). The papers were allowed to dry and then folded into envelopes in which approximately 50 cattle tick (*B. microplus*) larvae were enclosed. The envelopes were held at 25°C and >80% RH for 48 h. The percentage mortality of tick larvae was then recorded and compared with that of the controls.

Gravid female injection test. Test compounds were dissolved in dimethylsulfoxide and, using a microapplicator, 2 μl of the solution were injected into the blood-filled stomach of a tick (*B. microplus*) giving application rates of 20, 10, 3 and 1 μg per tick. Five replicate ticks were treated at each concentration and subsequently each tick was retained separately in partitioned dishes held at 25°C and >80% RH, until mortality of ticks or fecundity and viability of eggs produced by survivors could be assessed. The percentage reduction in total reproductive capacity (i.e. the combined effects of adult mortality, reduced fecundity and mortality of eggs) was then recorded and compared with that of controls which had been injected with solvent alone (2 μl).

TABLE 3
Activities of Substituted 2-Aryl-1,2,3-triazoles against Four Insect Species

	Activity against				
	B. microplus				
Compound	*Larval*[a]	*Reproductive*[b]	L. sericata[a]	M. domestica[c]	B. germanica[c]
11	10–30	20	30	10	100
12	3–10	20	10–30	0·3–1	3
13	100	3–10	30–100	30–100	0·3–1
14	Inactive	—	10–30	30	—
15	10–30	10	10	0·3–1	3–10
16	10–30	3	30–100	1	30–100
17	100	Inactive	10–30	10	—
18	30–100	20	Inactive	1	3–10
19	100	Inactive	Inactive	1–3	3
20	Inactive	20	300	10–30	Inactive
21	Inactive	10–20	Inactive	Inactive	—
22	30–100	3–10	10–30	10	—
23	30	3	10–30	100	1–3
24	Inactive	20	100–300	Inactive	—
25	Inactive	Inactive	100	30–100	—
26	100–300	20	100–300	30	—
27	30–100	1	3	30–100	0·1
28	10–30	20	10	0·3–1	10–30
29	Inactive	Inactive	100	3	100
30	Inactive	Inactive	100	10	Inactive
31	30	3	3	0·3–1	10–30
32	30–100	3	10–30	10	—
33	30	1	3	10	3–10
34	300	20	Inactive	Inactive	—
35	100	3–10	3–10	100	—
36	100	3–10	3	30–100	—
37	Inactive	Inactive	Inactive	30	—
38	Inactive	Inactive	Inactive	Inactive	—
39	Inactive	Inactive	Inactive	Inactive	—
40	Inactive	Inactive	300	1	30–100
41	30–100	Inactive	30	1	10–30
42	100	10–20	100	300	—
43	100	Inactive	30–100	30–100	—
44	Inactive	Inactive	Inactive	300–1000	—
45	Inactive	10	Inactive	100–300	—
46	30–100	Inactive	30	10–30	3
47	100	3–10	30	30	—
48	Inactive	Inactive	100	1000	—
Fipronil	10	<20	0·3	10–30	—
Permethrin	30	—	3	300	1·5

[a] = LD_{50} in mg litre^{-1}.
[b] = ED_{50} in μg per tick.
[c] = LD_{50} in mg m^{-2}.

2.2.2 Sheep blowfly (Lucilia sericata)
One-millilitre aliquots of acetone solutions or suspensions, containing test compound at various concentrations (300, 100, 30, 10, 3, 1 mg litre^{-1}), were applied to cotton-wool dental rolls (1 × 2 cm) contained in glass vials 2 cm diameter × 5 cm long. After drying, the treated rolls were impregnated with 1 ml of nutrient solution and infested with approximately 30 first-instar larvae of sheep blowfly (*L. sericata*). The vial was closed by a cotton-wool plug and held at 25°C for 24 h. The percentage mortality of the insects was then recorded.

2.2.3 Housefly (Musca domestica)
Aliquots (0·7 ml) of acetone solutions or suspensions of test compounds at various concentrations were applied to filter papers (9 cm diameter) placed in the bottom of

petri dishes (9 cm diameter). Applications rates were 1000, 300, 100, 30, 10, 3, 1 and 0·3 mg m^{-2}. After evaporation of solvent, the treated surfaces, together with controls treated with acetone alone, were then infested with adult houseflies (*M. domestica*). The dishes were closed by glass lids and held at 22°C for 24 h. The percentage mortality of the insects was then recorded.

2.2.4 Cockroach (Blattella germanica)
Aliquots (1 ml) of solutions or suspensions of test compounds in acetone were applied to glass plates (10 × 10 cm) to give applied rates of 100, 30, 10, 3, 1 and 0·1 mg m^{-2}. After evaporation of solvent, the treated surfaces, together with controls treated with solvent alone, were then infested with 10 first-instar nymphs of the German cockroach (*B. germanica*). These were retained on the treated surface within PTFE-coated glass rings 6 cm in diameter and held for 24 h at 25°C. The percentage mortality of the insects was then recorded.

The biological results are tabulated in Table 3. When a range is shown, e.g. 10–30, the compound is generally 100% active at the higher rate and inactive at the lower rate.

3 DISCUSSION

The biological results for compounds **12** and **42–46** show that the 2,6-dichloro-4-trifluoromethyl substitution pattern on the aryl ring appears to be vital for broad-spectrum activity. Replacement of the 4-trifluoromethyl group in compound **12** with 4-trifluoromethylthio, as in **46**, reduces the activity against all organisms except cockroaches. The 2,4,6-trichloro compound **42** is considerably less active than **12** as is compound **43** where the chlorine substituents have been replaced by bromine. The polyfluoro substituted compounds **44** and **45** were also only weakly active.

Within that group of compounds, differences in stability and physical properties could contribute to differences in activity. However, compounds **31**, **47** and **48** have similar properties but very different activities which, could be ascribed to differences in intrinsic activity at the site of action. As in related insecticides, these compounds are thought to act on the GABA-activated chloride channel.[9] Relative activities of 1000 : 10 : 1 of compounds **31** (2,6-Cl_2, 4-CF_3), **47** (2,6-Cl_2, 4-OCF_3) and **48** (2,4,6-Cl_3) in the GABA test are directly reflected in their *M. domestica* LD_{50} values of 0·3–1, 30 and 1000 mg m^{-2} and topical LD_{50} values of 0·1, 1 and 10 μg per fly.

On the triazole ring, both electron-withdrawing and electron-donating groups are tolerated at position **5**, while hydrogen or methyl is favoured at position **4**. Fluorine substitution on the thiomethyl group of **12** to give compounds **15–17** retains much of the activity, as does replacement of thiomethyl by cyano. Methoxy and dimethylamino replacements are considerably less active.

Interpretation of the structure–activity relationships, especially against houseflies and cockroaches, is complicated by the opposite effects of volatility of the compounds in the two tests. Vapour effects on neighbouring untreated controls were noticed with some compounds and the more volatile compounds were active on houseflies but not cockroaches.

In the housefly test, the treated surface can be avoided by resting on the walls or lid of the Petri dish and exposure is largely through the vapour phase in a way similar to the experiments of Nicholls *et al.* with soil insecticides.[10] Fipronil and permethrin are poorly active in this test, as is compound **27** despite GABA activity equal to that of compound **31** and a topical LD_{50} to houseflies of 0·1 μg per fly.

In the cockroach test on an open plate, exposure is by contact with the residual deposit and any vapour is immediately lost, so reducing the remaining deposit and favouring the less volatile compounds. Permethrin, the sulfone **13** and the dimethylsulfamoyl compound **27** are the most active in this test.

Measurements of the loss of compounds **31** and **35** from glass gave loss rates of 2–4 mg m^{-2} h^{-1} and less than 5×10^{-3} mg m^{-2} h^{-1}, respectively, in good agreement with calculated values.[11] Persistence tests against houseflies and cockroaches at 100 mg m^{-2} gave residual activity consistent with calculated volatilisation rates. Compound **30**, estimated to lose over 100 mg m^{-2} h^{-1}, gave no residual activity while the non-volatile sulfonyl and sulfamoyl compounds **13** and **27** gave control for over five weeks.

These vapour effects explain some of the structure–activity effects such as the decrease in housefly activity on oxidation of thioethers. Compound **31**, as would be expected from an unhindered aliphatic thioether, is very readily oxidised in biological systems to the sulfoxide **35** which is possibly the actual toxicant and has similar activity except against houseflies.

In summary, these 2-aryl-1,2,3-triazoles represent a new series of potent insecticides, in which a wide range of substituents is tolerated on the triazole ring, and the preferred aryl substitution pattern is 2,6-dichloro-4-trifluoromethyl. Of this series, 2-(2,6-dichloro-4-trifluoromethylphenyl)-4-methyl-5-methylthio-2*H*-1,2,3-triazole (**12**) has the best combination of potency, broad spectrum and residual activity. This compound gave outstanding control of houseflies, good control of cattle ticks and sheep blowflies and moderate control of cockroaches.

ACKNOWLEDGEMENTS

The authors thank Dr Harald C. von Keyserlingk (Schering AG, Berlin) for housefly GABA tests.

REFERENCES

1. Rhone-Poulenc, *European Patent* 295 117, 1988.
2. Colliot, F., Kukorowski, K. A., Hawkins, D. W. & Roberts, D. A., *Proc. Brighton Crop Prot. Conf.—Pests and Diseases*, **1** (1992) 29–34.
3. Whittle, A. J., 3-Aryl pyrimidinones: a novel class of potent insecticides. In *Advances in the Chemistry of Insect Control III*, ed. G. G. Briggs. Royal Society of Chemistry, 1994, pp. 156–70.
4. Schering Agrochemicals Ltd, *European Patent* 350 237, 1990.
5. Begtrup, M. & Holm, J., Electrophilic and nucleophilic substitution in the triazole *N*-Oxides and *N*-methoxytriazolium salts: preparation of substituted 1,2,3-triazoles, *J. Chem. Soc., Perkin Trans. 1* (1981) 503–13.
6. Begtrup, M., 1,2,3-Triazoles produced from 5-substituted *N*-methoxytriazolium salts. *J. Chem. Soc., Perkin Trans. 1* (1982) 2749–56.
7. Begtrup, M., Introduction of substituents into 5-membered aza-hetercycles. *Bull. Soc. Chim. Belg.*, **97** (1988) 573–97.
8. Swartz, D. L., Karash, A. R., Berry, L. A. & Jaeger, D. L., Synthesis of some 4-substituted-2-(*o*-halogenophenyl)-1,2,3-triazoles. *J. Heterocyclic Chem.*, **20** (1983) 1561–4.
9. von Keyserlingk, H. C. & Willis, R. J., The GABA-activated Cl^- channel in insects as target for insecticide action: a physiological study. In *Neurotox '91: Molecular Basis of Drug and Pesticide Action*, ed. I. R. Duce. Elsevier Applied Science, London and New York, 1991, pp. 79–104.
10. Nicholls, P., Farnham, A. W. & Buxton B., *Proc. Brit. Crop Prot. Conf.—Pests and Diseases*, **1** (1981) 175–82.
11. Briggs, G. G., Predicting the behaviour of pesticides in soil from their physical and chemical properties. *Phil. Trans. R. Soc. Lond. B*, **329** (1990) 375–82.